# Solubility of Some Metal Fluorides in Bromine Trifluoride

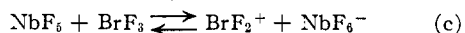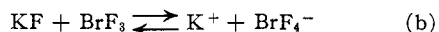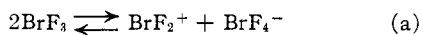BY IRVING SHEFT, HERBERT H. HYMAN AND JOSEPH J. KATZ

The solubility of a number of the metal fluorides in bromine trifluoride has been determined at 25° and at 70°. These solubilities are compared with solubilities in water and anhydrous hydrogen fluoride. The data are correlated by considering the behavior of these fluorides as fluoride ion donors or acceptors. The ability to donate or accept fluoride ions is related to the position of the element in the periodic table and especially to its oxidation state, and enables the solubility characteristics of the metal fluorides to be readily systematized.

## Introduction

Interest has recently been aroused in the properties and reactions of bromine trifluoride. Eméleus and his co-workers have reported a number of the reactions and have discussed the nature of bromine trifluoride solutions.[1-3] Bromine trifluoride is an ionizing solvent with a high electrical conductivity.[4,5] Eméleus has dealt with the qualitative aspects of bromine trifluoride as a solvent for fluorides at some length. Bromine trifluoride may act both as a fluoride ion acceptor and donor in an acid-base type solvent system in which the fluoride ion plays a role analogous to that of the proton in water though reversed in charge. This is illustrated in the equations

$$2BrF_3 \rightleftarrows BrF_2^+ + BrF_4^- \qquad (a)$$
$$KF + BrF_3 \rightleftarrows K^+ + BrF_4^- \qquad (b)$$
$$NbF_5 + BrF_3 \rightleftarrows BrF_2^+ + NbF_6^- \qquad (c)$$

The right side of these equations indicates the ionic species present in solution. The solid in equilibrium with the solution is determined by other considerations.

The alkali metal fluorides are soluble and essentially completely ionized. The solubility increases as the size of the cation increases. As the valence number increases in going across the periodic table, the effective nuclear charge increases, and therefore the tendency to lose fluoride ions decreases. As a result the solubility in bromine trifluoride decreases. However, since bromine trifluoride also functions as a fluoride ion donor, the solubility rises sharply when those fluorides are reached which can act as fluoride ion acceptors. Such fluorides are typically the group V fluorides, $MF_5$, which dissolve in bromine trifluoride to give strongly conducting solutions in which the ionic species are probably $BrF_2^+$ and $MF_6^-$.

Hexavalent elements form volatile fluorides, e.g., sulfur hexafluoride, molybdenum hexafluoride and tungsten hexafluoride, which are also readily soluble in bromine trifluoride. In general, however, the solubilities of these compounds appear to be related to their melting points so that bromine trifluoride may be regarded in these cases as an inert solvent and no dissociation or donor mechanisms need be involved. This paper deals with the quantitative solubility of a number of metal fluorides in bromine trifluoride. The compounds investigated

(1) A. G. Sharpe and H. J. Eméleus, J. Chem. Soc., 2135 (1948).
(2) H. J. Eméleus and A. A. Woolf, ibid., 164 (1950).
(3) H. J. Eméleus and A. A. Woolf, ibid., 1050 (1950).
(4) A. A. Banks. H. J. Eméleus and A. A. Woolf, ibid., 2861 (1949).
(5) A. A. Woolf and H. J. Eméleus, ibid., 2865 (1949).

include fluorides of elements from valence numbers I through V and show a wide range of solubilities.

## Experimental

**Materials.**—The bromine trifluoride used in these experiments was obtained from the Harshaw Chemical Company and purified by vacuum distillation in an all nickel still. The major impurities are bromine, bromine pentafluoride, hydrogen fluoride and non-volatile fluorides and are readily separable by distillation. The fraction used (b.p. 95–95.5° (250 mm.)) was pale yellow in color and was stored in a nickel container. The time interval between distillation and use was generally less than three to four days.

The lithium fluoride, sodium fluoride, potassium fluoride, aluminum fluoride and barium fluoride were J. T. Baker Analyzed, Baker and Adamson, or Merck reagent grade chemicals. They were dried and pretreated with bromine trifluoride before use. Silver fluoride was a technical grade from the City Chemical Company, New York, and was similarly treated. Copper fluoride was prepared from reagent grade copper fluoride dihydrate by dehydrating with bromine trifluoride and drying under vacuum. Cesium fluoride was prepared from an available sample of specially purified cesium bromide, which was spectroscopically free of the other alkali metals, by treating with bromine trifluoride and drying. Nickel fluoride was similarly prepared from nickel chloride dihydrate. Zirconium fluoride was prepared from an available sample of very pure zirconium tetrachloride–phosphorus oxychloride complex by treating with bromine trifluoride in an analogous fashion. Chemical analysis showed the product to be over 90% zirconium tetrafluoride. Lanthanum fluoride and thorium fluoride were made by reaction of aqueous hydrofluoric acid on the appropriate nitrate, centrifuging, drying and pretreating with bromine trifluoride. Niobium pentafluoride was prepared from niobium pentoxide and bromine trifluoride. The volatile impurities, e.g., hydrogen fluoride and bromine, were removed under vacuum and the resulting slurry was used as such.

**Equipment.**—The solubility apparatus is shown in Fig. 1. The apparatus was contained in a constant temperature air box. The temperature of the box was maintained constant to ±0.75° at 25° and to ±0.40° at 70°. The air temperature was uniform throughout the box to ±0.10°. During the equilibration the entire box was placed on a rocker. The equipment is rather conventional, although fritted Fluorothene, a new filter medium, was employed. The fritted Fluorothene was obtained in sheets from the Carbon and Carbide Laboratories, Oak Ridge, and had a pore size of 5 microns. Disks $^7/_8$ inch in diameter were cut and inserted into tight fitting, thin walled, copper rings which were $^1/_5$ inch deeper than the thickness of Fluorothene. The extra wall was then spun down on the filter to give a liquid tight seal. In several duplicate experiments, a sintered nickel filter of pore size about 5 microns was used in series with the standard Fluorothene filter and no change in solubility was noted.

**Experimental Technique.**—Excess metal fluoride and purified bromine trifluoride were mixed in a quartz tube. This tube was given a short evacuation to remove bromine and hydrogen fluoride without removing much bromine trifluoride. The residual slurry was then poured into the copper mixing tube. The solubility apparatus was assembled in an inverted position and placed in the constant-temperature box, which was lying on the rocker platform, The rocker was shaken for approximately 20 hours during equilibration. The displacement was such that at no time
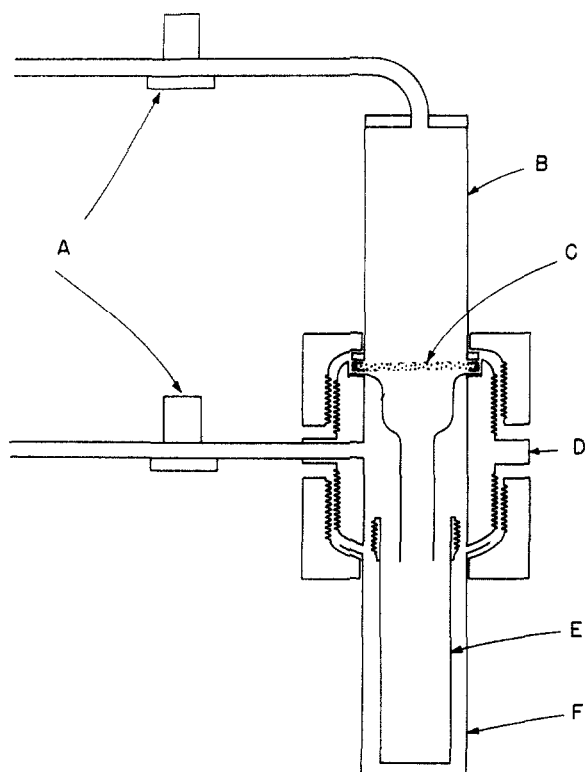
Fig. 1.—Solubility apparatus: A, crane bellows valve; B, copper mixing tube; C, fritted Fluorothene filter in copper holder; D, brass $^3/_4"$ union; E, Fluorothene weighing tube; F, Fluorothene tube.

could liquid come in contact with the filter. After equilibration, the box was turned upright, the lower valve opened, and helium pressure applied through the top valve to force the saturated solution through the filter into the weighed collecting tube. The lower half of the apparatus was opened and the collecting tube sealed with a Fluorothene cap and weighed. The excess bromine trifluoride was removed under vacuum,[6] and the residue analyzed for the metal in question.

Lithium was determined spectrographically. Sodium was precipitated with magnesium uranyl acetate and weighed as sodium uranyl acetate. Potassium and cesium were determined gravimetrically as perchlorates. Silver was determined as the chloride and barium as the sulfate. Calcium was precipitated as the oxalate and titrated with permanganate. Copper, nickel and zirconium were determined colorimetrically with diethyldithiocarbamate, dimethylglyoxime and p-dimethylaminoazophenylarsonic acid, respectively. Aluminum and lanthanum were precipitated with ammonium hydroxide and ignited to the oxide. Niobium was precipitated with cupferron and ignited to the oxide. Thorium was determined gravimetrically as the oxalate.

### Results and Discussion

The data obtained are summarized in Table I. The actual determinations were made by analysis of a known weight of solution for a specific metal ion, and the data in columns 2 and 4 are calculated directly. It is interesting to compare the solubilities of these fluorides in bromine trifluoride with their solubility in water and anhydrous hydrogen fluoride. To compare solubilities between different salts and different solvents, certain assumptions must be made as to the species in solution.

(6) During the evacuation of the niobium solution, a white sublimate collected throughout the vacuum line. Since this could lead to loss of Nb, the filtered NbF₅ solution was hydrolyzed in toto for analysis.

In the case of bromine trifluoride, an assumption has been made in accordance with the qualitative viewpoint adopted by Eméleus and discussed in the introduction. Bromine trifluoride can function as either a fluoride ion donor or acceptor, depending on the metal fluoride in solution. The cations formed from univalent metals (and barium) are presumed to be unsolvated while the anion in solution is $BrF_4^-$. In the case of aluminum and those elements which show even more limited solubility, no conclusions have been drawn regarding the species in solution. The relatively small tendency to either accept or donate a fluoride ion to bromine trifluoride is reflected in their low solubility.

The solubilities in water are calculated as simple unsolvated metal fluorides. This is clearly inadequate for salts such as nickel and aluminum fluoride where complexes of at least moderate stability must exist in solution. It probably is not unreasonable for the alkali metal fluorides. The solubility and its relationship to atomic size may be accounted for by the strong ionic character of the fluoride bonds and the high dielectric constant of water.

In hydrogen fluoride solutions we have chosen to emphasize the role of the solvent as a fluoride ion acceptor. The solubilities are calculated for unsolvated cations with $HF_2^-$ as the principal anion.

In comparing the solubility in the three solvents we consider first the univalent fluorides. All of these except lithium fluoride are relatively soluble in all three solvents and show a positive temperature coefficient of solubility in bromide trifluoride. In the absence of data on activity coefficients for these strong electrolytes in concentrated solution, or even reliable information as to the ionic species in solution, no reasonable heats of solution can be calculated. In the case of potassium fluoride and silver fluoride the solids in equilibrium appear to be solvated, and the heat absorbed in solution is only that required to dissociate the ionic lattice. In the case of sodium and cesium, the solids in equilibrium probably are not solvated. In addition to the heat absorbed in dissociation of the ion pairs, the heat evolved in the production of $BrF_4^-$ from $BrF_3$ and $F^-$ would be included in the heat of solution. The net effect is apparently absorption of heat and a positive temperature coefficient of solubility.

Lithium fluoride, calcium fluoride and barium fluoride are substantially more soluble in hydrogen fluoride and bromine trifluoride than in water. This is probably related to the behavior of the fluorine containing solvents as fluoride ion acceptors. In the case of calcium fluoride and lithium fluoride the solid phase in equilibrium with the bromine trifluoride solution is probably not solvated. These salts show a lower solubility at 70° than at 25°, and therefore the solution of lithium fluoride and calcium fluoride is exothermic. Unlike the situation with respect to sodium and cesium, the heat liberated during dissolution by the formation of the $BrF_4^-$ from $BrF_3$ and $F^-$ is greater than the heat of fusion of the salts and the dissociation of the ion pairs.

In the case of barium fluoride where the solid

TABLE I

SOLUBILITY OF METAL FLUORIDES IN BROMINE TRIFLUORIDE, WATER AND HYDROGEN FLUORIDE

| Metal (M) | Bromine trifluoride 25° g. M/100 g. soln.[a] | Mole fraction × 100 | Bromine trifluoride 70° g. M/100 g. soln.[a] | Mole fraction × 100 | Water[d] 25° Mole fraction × 100 | Hydrogen fluoride[e] 12° Mole fraction × 100 |
|---|---|---|---|---|---|---|
| Type MF | | $MBrF_4$[c] | | | MF[c] | $MHF_2$[c] |
| Li | 0.125 ± 0.003 | 2.5 | 0.081 ± 0.007 | 1.6 | 0.1 | 7.7 |
| Na | 2.08 ± .2 | 12.9 | 2.55 ± .002 | 15.8 | 1.8 | 13.8 |
| K | 4.73 ± .01 | 17.9 | 5.38 ± .03 | 20.5 | 24.2 | 12.9 |
| Ag | 3.22 ± .3 | 4.2 | 4.08 ± .005 | 5.5 | 20.0 | 12.5 |
| Cs | 18.8 ± 1.0 | 24.7 | 19.5 ± .2 | 25.9 | 35.0(18°) | 25.2 |
| Type $MF_2$ | | $M(BrF_4)_2$[c] | | | $MF_2$[c] | $M(HF_2)_2$[c] |
| Ca | 0.017 ± 0.009 | 0.1 | <0.001 | | 0.0004 | 0.2 |
| Ni | <0.002 | | <0.001 | | .5(20°) | 0.008 |
| Cu | <0.002 | | | | .01 | 0.002 |
| Ba | 3.53 ± 0.2 | 3.9 | 5.16 ± 0.07 | 5.8 | .01 | 1.3 |
| Type $MF_3$ | | | | | $MF_3$[c] | $M(HF_2)_3$[c] |
| Al | 0.0195 ± 0.0002 | [b] | 0.0038 ± 0.0003 | [b] | 0.12 | 0.0004 |
| La | <0.02 | | <0.02 | | ... | ... |
| Type $MF_4$ | | | | | $MF_4$[c] | $M(HF_2)_4$[c] |
| Zr | <0.0005 | [b] | <0.001 | [b] | 0.16 | 0.001 |
| Th | <0.001 | | ... | | 0.01 | 0.0004 |
| Type $MF_5$ | | $BrF_2MF_6$[c] | | | | |
| Nb | 15.7 ± 0.01 | 34.1 | ... | | ... | ... |

[a] Average of several determinations. Errors are average deviations. [b] Not calculated because ionic species not known. [c] Species assumed in making calculation. [d] Calculated from Seidell, "Solubilities," D. Van Nostrand Co., Inc., New York, 1940, $ZrF_4$ is from Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 7, Longmans, Green and Co., London, 1910, p. 138. [e] Calculated from data by Jache and Cady, *J. Phys. Chem.*, **56**, 1106 (1952).

phase has been shown by Emeléus to be $Ba(BrF_4)_2$, the behavior is identical with that of potassium and silver fluorides and the solubility increases with increasing temperature. Barium, potassium and silver are reported to form stable solid bromofluorides, while sodium and cesium do not.[1] Since in all cases the anion in solution is probably $BrF_4^-$, the formation of stable solid bromofluorides is related to the size of the cation in the crystal lattice. The crystal radii[7] of those ions which do form stable bromofluorides are very close to the 1.36 Å. radius of fluorine, and it could be this similarity that is important in the formation of stable crystals. Since the only other common ion having a comparable radius is $Au^+$ (1.37 Å.) which is oxidized in bromine trifluoride to the acid $BrF_2AuF_4$,[8] it would seem unlikely that other stable bromofluorides with structures of this type will be isolated.

The behavior of aluminum fluoride appears to fit a slightly different pattern. It is probably a weak fluoride ion acceptor and an extremely weak fluoride donor, a characteristic of elements in the middle region of each period. This explains its insolubility in hydrogen fluoride and its significantly higher solubility in bromine trifluoride with a negative temperature coefficient of solubility. The existence of aquo complexes as well as fluoride ion complexes may account for the moderate solubility of fluorides like aluminum fluoride, nickel fluoride and zirconium fluoride in water.

The high solubility of niobium pentafluoride in bromine trifluoride certainly illustrates a case in which bromine trifluoride is a fluoride ion donor and the salt an acceptor. We would anticipate very limited solubility in anhydrous hydrogen fluoride. Antimony pentafluoride is reported as insoluble and $NaNbF_6$ is reported as soluble in anhydrous hydrogen fluoride[9] although there appear to be no data on the solubility of $NbF_5$.

(7) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 346.

(8) A. G. Sharpe, *J. Chem. Soc.*, 2901 (1949).

(9) J. H. Simons, ed., "Fluorine Chemistry," Vol. 1, Academic Press, Inc., New York, N. Y., 1950, p. 235.